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13. ABSTRACT (Maximum 200 words)

The research activities of our MURI focused on the use of dendritic polymers in materials applications. The research concentrated in four main areas: bulk properties, devices, advances in computational methods for modeling and smulation of dendrimers, and chemical properties. The area of bulk properties addressed issues relating to fundamental and technological aspects of dendrimers for their intrinsic properties or ability to modify other materials in mass quantity. Examples of research in this area included the search for new high performance hyperbranched polymers, novel approaches to control macromolecular architecture, and the study of blends of dendritic materials with commodity polymers to facilitate processing and enhance the performance of traditional polymeric materials. The area of devices focused on using dendritic materials as active components in sensors. Augmenting all of the research was the development of new computational methods for simulating dendritic materials. The team combined strengths in synthesis, molecular modeling and computation, and characterization to capitalize on the materials opportunities offered by this unusual family of polymers. Finally, the area of chemical properties addressed dendrimers in applications that involved molecular recognition and catalysis.

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Enclosure 1

DENDRITIC MATERIALS SYSTEMS FINAL PROGRESS REPORT (Jeffrey Moore, PI)

2.b.2. Table of Contents

2.b.4. Statement of the problem studied

The research activities of our MURI focused on the use of dendritic polymers in materials applications. The research was concentrated in four main areas:

- bulk properties
- devices
- advances in computational methods for modeling and simulation of dendrimers
- chemical properties

The area of bulk properties addressed issues relating to fundamental and technological aspects of dendrimers for their intrinsic properties or ability to modify other materials in mass quantity. Examples of research in this area included the search for new high performance hyperbranched polymers, novel approaches to control macromolecular architecture, and the study of blends of dendritic materials with commodity polymers to facilitate processing and enhance the performance of traditional polymeric materials. The area of devices focused on using dendritic materials as active components in sensors. Augmenting all of the research was the development of new computational methods for simulating dendritic materials. The team combined strengths in synthesis, molecular modeling and computation, and characterization to capitalize on the materials opportunities offered by this unusual family of polymers. Finally, the area of chemical properties addressed dendrimers in applications that involved molecular recognition and catalysis.

2.b.5. Summary of the most important results

A. TERMINI

The TERMINI (*Irreversible TERminator Multifunctional INItiator)* project developed a novel method for the synthesis of dendritic macromolecules from commercially available monomers. These materials combined the low cost of common monomers with the architectural complexity and interesting properties of dendritic macromolecules providing a potentially unlimited pool of materials characterized by a broad range of properties and applications. The concept behind this method takes advantage of the known, facile, safe and high yield methodologies developed in our laboratory. By a combination of a metal-catalyzed living radical polymerization, a quantitative (and irreversible) reaction with TERMINI agent, and an oxidative chlorination process, access to a new class of dendritic macromolecules was gained.

B. Polyetherimide Hyperbranched Polymers

We synthesized and studied a new type of AB2 hyperbranched polyetherimides prepared from readily available monomers. As an extension of that research, end-group modified hyperbranched polyetherimides were prepared by a one-pot, two-step reaction sequence. General synthetic techniques were developed to prepare both monofunctional terminating segments and the corresponding modified polyetherimide hyperbranched polymers. Monofunctional groups were used to terminate an AB2-type polycondensation reaction, generating capped hyperbranched polymers(HBPs). The composition and constitution of the end groups controlled the solubility and thermal properties of the HBPs. For the same polymer backbone, different end groups were able to shift the glass-transition temperature nearly100 °C. Endgroup modification greatly influenced the film-forming ability of the HBPs in thick film applications with long endgroups capable of chain entanglements providing uniform continuous films.

We found that the surface properties of polyetherimide (PEI) hyperbranched polymers (HBPs) are tunable over a broad range of surface energies by proper functionalization of their end-groups. Our data indicated that the surface segregation of PEI HBPs in blends with polystyrene (PS) was primarily determined by the differences in their surface energies. Therefore, HBPs with higher surface energies than that of PS segregated near the substrate, while HBPs with lower surface energies tended to concentrate near the air interface of thin films. This preferential segregation was shown to dramatically affect the de-wetting behavior of the PS blends.

C. Dendritic Polymer Blends

Two studies were carried out concerning dendritic-polymer blends and the effects of end groups in materials and processing properties. In the first study, we investigated the behavior of hyperbranched polyetherimides, functionalized with various end-groups, in blends with linear polystyrene (PS). The endgroup composition of the HBPs was correlated with changes in surface energy that consequently affected the surface segregation properties of the HBP/PS blends. The latter, in turn, were correlated with the stability (wettability) of thin PS films on silicon wafers. The wettability of low molecular weight PS thin films on the silicon substrate was improved by the addition of high surface energy PEI HBPs.

In the second, related study, we investigated the influence of alkyl end groups on the miscibility of HBPs with polyolefins. In particular, polyetherimide (PEI) hyperbranched polymers with alkyl terminated end-groups were blended with linear low density polyethylenes (LLDPEs) and extruded as thin films. The effects of length and concentration of the alkyl groups on the miscibility of the extruded films were examined using confocal and scanning electron microscopy (SEM). Surface properties of the blends were further characterized using contact angle measurements in de-ionized water. Results indicated that migration of PEI HBPs to the film surfaces was predominantly driven by the surface energy differences of HBPs and polyolefins. Moreover, the addition of PEI HBPs to LLDPEs had a negligible effect on the processing properties of LLDPEs.

D. Polymer Imprinting

We developed a “monomolecular imprinting” approach, which contained elements of both the DCL and covalent imprinting approaches, and produced macromolecular hosts containing a single bind site. This monomolecular imprinting strategy had several appealing features. The first was the use of the RCM reaction, which forms robust carbon-carbon double-bond cross-links but is nonetheless reversible. The ability to equilibrate cross-link isomers potentially allows the dendritic framework to reach a lowest-energy “mold” around the template. Perhaps more importantly, this strategy produced sizeable macromolecular hosts (MW ! 10 kDa) but with a single imprinted site per molecule. Although there was no evidence of heterogeneity in this system, in cases where mixed imprints do arise the potential exists for fractionating. In this regard, the ability to select hosts based on binding kinetics, selectivity, or affinity would be quite powerful.

E. Dendron Rodcoils

We developed a family of molecules consisting of three blocks, a dendritic segment, a rod-shape aromatic segment, and a flexible coil-like segment. These triblock molecules were referred to as dendron rodcoils (DRCs). Very dilute solutions of DRC molecules in certain solvents, such as styrene, 2-ethylhexyl methacrylate (EHMA), dichloromethane, and chloroform, undergo spontaneous gelation due to the formation of three-dimensional networks of self assembled DRC nanoribbons. These nanoribbons have widths of about 10 nm, a thickness in the range of 2 nm, and lengths on the order of microns, as revealed by small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The self assembled gels are birefringent due to the order parameter in the DRC nanoribbon networks trapping solvent molecules. Also studied was the capacity of these DRC molecules to self assemble into one dimensional structures that can act as scaffolds for some polymers and significantly improve their orientability under mechanical forces. The high ratio of monomer to DRC scaffold molecules implies an enormous contact area between the scaffold and the polymer matrix and a nanoscaffold weaving through the matrix.

2.b.6.a. Publications – papers published in peer-reviewed journals

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2.b.6.b. Publications – papers published in non-peer-reviewed journals or in conference proceedings
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V. Percec, B. Barboiu, B. B. De, H. –J. Kim, J. D. Smith, M. van der Sluis, B. H. Grubbs and J. M. J. Fréchet. "Self – Regulated Metal Oxides Catalyzed Living Radical Polymerization Initiated with Multifunctional Sulfonyl Chlorides," *Polym. Prepr.* p. 457.

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Harth, E., Bosman, A., Benoit, D., Helms, B., Fréchet, J.M.J., Hawker, C.J. "A practical approach to the living polymerization of functionalized monomers: application to block copolymers and 3-dimensional macromolecular architectures" Macromolecular Symposia, 2001, 174, 85-92.

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Book Chapters

Chou, J.-H.; Kosal, M. E.; Nalwa, H.S.; Rakow, N.A.; Suslick, K. S. "Applications of Porphyrins and Metalloporphyrins to Materials Chemistry" in *The Porphyrin Handbook*, Kadish, K.; Smith, K.; Guilard, R., ed.; Academic Press: New York; vol. 6, ch. 41, pp. 43-131, (2000).

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2.b.6.c. Publications – papers presented at meetings, but not published in conference proceedings

An abstract was submitted to the Solid State Sensor and Actuator Workshop 2000 held at Hilton Head Island, SC. If accepted, this technology will be presented at the conference that is to be held on June 4-8, 2000.

2.b.6.d. Publications – manuscripts submitted but not published

L. Li, E. Beniash, E. R. Zubarev, W. Xiang, B. M. Rabatic, G. Zhang, and S. I. Stupp, “Assembling a Lasing Medium with Supramolecular Polymers and Crystals”, submitted for publication.

L. Li, J. C. Stendahl, G. Zhang, E. R. Zubarev, and S. I. Stupp, “One-Dimensional Dye-Orienting Self Assembled Nanoribbons,” to be submitted for publication.

2.b.6.e. Publications – technical reports submitted to ARO

Cagin, T.; Miklis, P.J.; Wang, G.; Zamanakos, G.; Martin, R.; Li, H.; Mainz, D.T.; Nagarajan, V.; Goddard, W.A. "Recent Advances in Simulation of Dendritic Polymers." Technical Report.

Deitzel, J.; Tan, N.B.; Kleinmeyer, J.D.; Rehrmann, J.; Tevault, D.; Reneker, D.; Sendijarevic, I.; McHugh, A.J. “Generation of Polymer Nanofibers Through Electrospinning”, ARL Technical Report, **1999** ARL-TR-1989, 1-33.

2.b.7. List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

Beebe	Hyuk-Jeen Suh (Ph.D., 2001) Hongmei Yu (grad)
Fréchet	Dr. Han-Ting Chang (postdoc) Dr. Dong Yu (postdoc) Dr. Todd Emrick (postdoc) Dr. Caiguo Gong (postdoc) W. Oldham Frantisek Svec (senior researcher) Dr. Marcelo Piotti (postdoc) Scott Grayson (grad) R. Kita (grad) Dr. Henrik Ihre (postdoc)

	Dr. Anton Bosman (postdoc) David Tully (grad) Catherine Liang (grad)
Goddard	Paul Miklis (?) Dr. Mamadou Diallo (staff) Dr. Tahir Cagin (staff) Dr. Daniel Mainz (postdoc) Dr. Yanhua Zhou (postdoc) Mr. Guofeng Wang (grad) Mr. Ryan Martin (grad) Mr. Georgios Zamanakos (grad) Nicholas Breen (undergrad) Dr. Prabhal Maiti (postdoc) Youyang Li (grad)
McHugh	Ibrahim Sendijarevic (Ph.D., 2002) Anand Lee (Ph.D., 2001) April Schricker (undergrad) Matthew Liberatore (grad)
Moore	Dr. P. Bharathi (postdoc) Peggy-Jean Prest (Ph.D., 1999) Josh Orlicki (Ph.D., 2002) Suresh Sriram (Ph.D., 2001) Larry Markoski (senior researcher) D. Scott Thompson (Ph.D., 2000) Zhengguo Zhu (Ph.D., 1999) Julie Thompson (Ph.D., 2003) Kevin Sill (B.S., 2001) Christian Ray (grad) Wei Zhang (grad)
Percec	Jason Smith (grad) Dr. Marcel van der Sluis (postdoc) Dr. P. Bissel Bogdan Barboiu (grad) Wook-Dong Cho (grad) S. W. Choi (grad) Dr. Tushar Kanti Bera (postdoc) Kun Si (grad) Marian Holerca (grad) Cris Grigoras (grad) Dr. Martin Glodde (postdoc)
Stupp	Dr. Eugene Zubarev (postdoc) Martin Pralle (Ph.D., 1999) Paul Braun (Ph.D., 1998) Dr. Sebastien Lecommandoux (postdoc) Dr. Janelle Gunther (postdoc) Dr. Harm-Anton Klok (postdoc)

	Mehmet Sayar (grad) Dr. Leiming Li (postdoc) Dr. Elia Beniash (postdoc) John C. Stendahl (grad) Bryan M. Rabatic (grad)
Suslick	Dr. M. Bhyrappa (postdoc) Neal Rakow (Ph.D., 2001) Dr. Avijit Sen (postdoc)
Zimmerman	Yoonkyung Kim (Ph.D., 2001) Michael Wendland (Ph.D., 2001) Dr. Denise Young (postdoc) Dr. Ilya Zharov (postdoc)

2.b.8. Report of Inventions (by title only)

1999

- A New Method for the Synthesis of Thermally Stable AmBn Polyetherimide Monomers and Polymers (m=1 or 2, when n=2 or 1 respectively) with Controlled Degrees of Branching (DB=0-1) and Easily Modified Endgroups that Determine Physical Properties. (Moore)

2000

- Dendritic Material Sacrificial Layer Micro-Scale Gap Formation Method. (Beebe/Moore)
- Microfabricated Devices and Method of Manufacturing the Same. (Beebe/Moore)
- Self-Assembling Compounds and use of the Same to Induce Order in Organic Media. (Stupp)

2001

- A Colorimetric Nose: 'Smell Seeing.' (Suslick)

2002

- Method of Creating Ribbon Polymer-Inorganic Nanocrystal Hybrid Ultraviolet Lasing Media Organized by Self Assembly and Electrophoresis. (Stupp)